

Origin of Polarity in Amorphous SrTiO₃

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Although neither SrTiO₃ nor BaZrO₃ has any polar crystalline polymorphs, they may form noncrystalline pyro- and piezoelectric phases [Adv. Mater. **19**, 1515 (2007)]. These phases and the similar phase of BaTiO₃ have been called quasiamorphous. In this Letter, the structure of the quasiamorphous phase of SrTiO₃ is examined by the x-ray absorption fine structure technique and found to be built of a random network of polar octahedral TiO₆ local bonding units. While in crystalline SrTiO₃ all TiO₆ octahedra are apex sharing only, in its amorphous and quasiamorphous phases, some octahedra share edges. The polarity of the quasiamorphous phase is due to the partial alignment of the TiO₆ octahedra. Such a mechanism is completely different from that of inorganic polar crystals. This mechanism should be possible in a large variety of other compounds that contain similar local bonding units.

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The recent discovery of the noncrystalline polar (called quasiamorphous) phases of SrTiO₃ and BaZrO₃ [1] represents the first known instance of materials that do not have polar crystalline polymorphs but do form noncrystalline phases which are polar. Existence of the quasiamorphous phases of SrTiO₃ and BaZrO₃ was predicted by the theory developed for the quasiamorphous phase of BaTiO₃ [2,3]. This theory states that in the amorphous state of these materials, there exists a random network (RN) of local bonding units (LBU), such as the TiO₆ octahedra in SrTiO₃ and BaTiO₃ and the ZrO₆ octahedra in BaZrO₃. In such a network, the local bonding units may be connected to each other in more than one way: apex-to-apex, edge-to-edge, or face-to-face. Therefore, the LBUs are distorted and possess local dipole moments. The network is stabilized by the presence of the divalent cations (Sr or Ba). The RN-LBU theory suggests that upon heating, the stability of the network is perturbed and some of the bonds between the LBUs are broken. In clamped thin films subjected to a strong temperature gradient, this process does not lead to crystallization but causes partial alignment of the LBUs, thereby imparting to the films a macroscopic polarization [2]. Thus, the amorphous nonpolar phase transforms into one, which is polar quasiamorphous. Here we use x-ray absorption fine structure (XAFS) analysis of amorphous, quasiamorphous, and crystalline films of SrTiO₃ to show definitively that (a) the TiO₆ LBU can be connected in more than one way, and (b) the transformation of the nonpolar amorphous into polar quasiamorphous phase is accompanied by structural changes involving the stabilizing cation (Sr or Ba). This experimental evidence is required to prove the validity and generality of the RN-LBU theory. In contrast to the previously studied BaTiO₃, where the Ti *K* edge and Ba *L*₃ edge overlap, thereby complicating quantitative analysis [3], XAFS studies of

SrTiO₃ are not hindered by an overlap between the Ti and Sr absorption edges.

For the current studies, amorphous 100 nm thick SrTiO₃ films were deposited by rf sputtering. The quasiamorphous form was obtained by pulling the as-deposited films through a temperature gradient with a peak temperature of 520 °C [1]. Polycrystalline films were prepared by annealing as-deposited films at 560 °C. The details of the experimental procedure are given in Refs. [4–6]. No indication of crystallinity was found in the amorphous and quasiamorphous films either by x-ray diffraction or by scanning electron microscopy (data not shown). Ti and Sr *K* edge x-ray absorption spectra of the SrTiO₃ thin films were measured in the fluorescence mode on beam line X11A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. Ti *K* edge spectra of EuTiO₃ powder measured on the same beam line (courtesy B. Ravel) were used as a reference. The experimental details were similar to those used previously for the XAFS investigation of BaTiO₃ [3].

The Ti x-ray absorption near edge structure (XANES) data of all samples contain a pronounced peak at 4967 eV corresponding to the *1s-3d* transition (peak *A*, Fig. 1). This transition is dipole-forbidden in the atom by the $\Delta L = 1$ selection rule [7] and not readily observable. However, if the final state of the photoelectron has some *p*-like character (e.g., via *p-d* mixture at the Ti site [8]) then the intensity of peak *A* is greatly enhanced, indicating that the local environment of Ti⁴⁺ is noncentrosymmetric [9]. Farges *et al.* [10], showed that the intensity and the energy of peak *A* fall within three distinct groupings depending on whether the coordination number of Ti is 4, 5, or 6 [3,10]. Although peak *A* observed for amorphous and quasiamorphous SrTiO₃ is shifted by 0.2 eV toward lower energies with respect to the quasiamorphous BaTiO₃ (Fig. 1), its

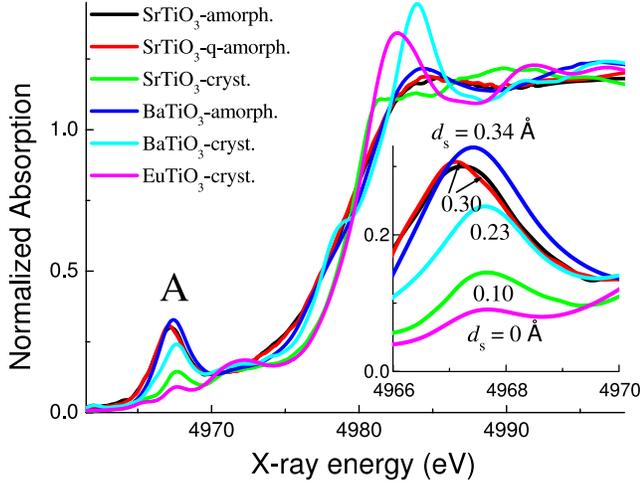


FIG. 1 (color online). Ti K edge XANES spectra of crystalline, amorphous and quasiamorphous SrTiO_3 . The data for amorphous, crystalline phase of BaTiO_3 (Ref. [2]) and bulk EuTiO_3 are given for comparison. Inset shows the peak A ($1s$ - $3d$ region), with average magnitudes of the Ti atom displacement.

position and intensity clearly place it within the domain of sixfold coordination (cf. Fig. 4 in Ref. [3]). Therefore, the Ti ion must be present in the distorted octahedral environment. For perovskites, the area of peak A is proportional to the square of the off-center displacement, d [11]

$$A = \frac{\gamma}{3} d^2, \quad (1)$$

where γ is a constant that, for the Ti ion, varies between 11.2 and 13.6 $\text{eV}/\text{\AA}^2$ [12,13]. The total off-center displacement, d , includes a dynamic contribution d_d , which is dominated by thermal vibrations [12,13] in nonpolar crystalline perovskites EuTiO_3 and SrTiO_3 , and a static

contribution d_s , caused by permanent loss of the inversion symmetry. The dynamic contribution is expected to be similar for all perovskite titanates at room temperature [10]. Therefore, the static contribution, d_s^{STO} , in SrTiO_3 can be determined by taking the difference of its peak area and that in EuTiO_3 at the same temperature ($\Delta A = A^{\text{STO}} - A^{\text{ETO}}$). Using the average value of $\bar{\gamma} = 12.4 \text{ eV}/\text{\AA}^2$, one obtains

$$\begin{aligned} d_s^{\text{STO}} &\approx \sqrt{(d_d^{\text{ETO}})^2 + 3\Delta A/\bar{\gamma}} - d_d^{\text{STO}} \\ &= \sqrt{(d_d^{\text{ETO}})^2 + 3\Delta A/\bar{\gamma}} - d_d^{\text{ETO}}. \end{aligned} \quad (2)$$

In amorphous and quasiamorphous thin films of SrTiO_3 the static displacement, $d_s^{\text{STO}} = 0.30 \text{ \AA}$, exceeds by far that found for $d_d^{\text{ETO}} = 0.103 \text{ \AA}$ in cubic EuTiO_3 . A small static off-center displacement in the crystalline SrTiO_3 ($d_s = 0.1 \text{ \AA}$, Fig. 1) is consistent with the previous report of 0.08 \AA [14] and can be attributed to the small deviation from cubic symmetry previously observed in thin films of SrTiO_3 [15]. The magnitude of d_s^{STO} implies local symmetry breaking leading to the existence of a strong, permanent dipole moment associated with each TiO_6 LBU.

A graph of the Fourier transform magnitudes of Ti K edge extended XAFS (EXAFS) data for the amorphous, quasiamorphous, and crystalline samples [Fig. 2(a)] as a function of distance, R , relative to Ti reveals two important features. (i) The peak corresponding to the first coordination shell Ti-O (1.4 \AA , uncorrected for the photoelectron phase shift) is preserved in all samples. This observation agrees with the XANES data that the TiO_6 octahedra, the LBUs of the crystalline phase of SrTiO_3 , are present in the amorphous and quasiamorphous phases as well. The decrease in intensity of this peak in the amorphous and quasiamorphous phases with respect to that in the crystal-

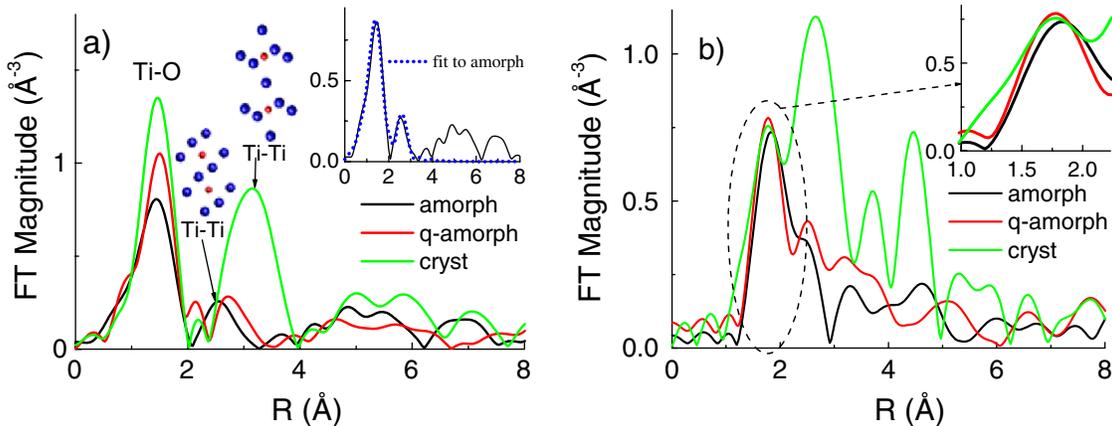


FIG. 2 (color online). Fourier transform magnitudes (uncorrected for the photoelectron phase shifts) of the k^2 -weighted EXAFS spectra of crystalline, amorphous and quasiamorphous SrTiO_3 : (a) the Ti edge EXAFS (k range from 2.5 to 9 \AA^{-1}). The inset shows fit to the amorphous SrTiO_3 data. The arrows point to the peaks corresponding to the two different types of connections shown by cartoons (edge-to-edge and apex-to-apex). The peak due to Ti-Sr bonds in the crystal overlaps that due to the Ti-Ti bonds. (b) Sr K edge (k range from 2 to 8.5 \AA^{-1}).

line phase can be attributed to the bond length disorder caused by Ti off-center displacement, which also agrees with the XANES data. (ii) The contribution of Sr-Ti and apex-sharing Ti-Ti (along with collinear Ti-O-Ti) bonds are not detectable in amorphous samples, though clearly visible in the spectrum of the crystalline SrTiO₃ [Fig. 2(a)]. This proves unambiguously that TiO₆ octahedra in amorphous samples do not form periodic linkages. The spectrum of the quasiamorphous phase is slightly different from that of the amorphous one only in the region characterizing the second-neighbor shell. This fact implies that the transformation from the amorphous to quasiamorphous phase does not cause significant changes to the TiO₆ octahedra but involves changes in the second-neighbor shell.

In the graph of the Fourier transform magnitudes of Sr *K* edge EXAFS for all three samples [Fig. 2(b)], the peak corresponding to the Sr-O shell in the amorphous and quasiamorphous samples (1.8 Å, uncorrected for the photoelectron phase shift) is slightly shifted and distorted with respect to the crystalline SrTiO₃ [Fig. 2(b) inset]. The peaks corresponding to the next neighbor shells are not well developed in the amorphous and quasiamorphous films of SrTiO₃ [Fig. 2(b)] but their FT magnitudes do differ from each other beyond the level of the noise [Fig. 2(b)]. These facts together imply that the local symmetry of the Sr environment in amorphous and quasiamorphous phases is lost and the transformation from the amorphous to quasiamorphous phase involves the rearrangement of the Sr ions in both the first and second coordination shells.

Noticeable optical and mechanical anisotropy of the quasiamorphous samples render quantitative analysis of the EXAFS spectra inconclusive. Therefore, the fitting of the EXAFS data was performed for only isotropic amorphous SrTiO₃ using IFEFFIT [16] and FEFF6 [17] packages (Table I). The Ti and Sr *K* edge EXAFS data were fit simultaneously, by constraining the Sr-Ti bond to have the same distance and disorder as measured at either

edge. The EXAFS amplitude reduction factors were determined from the fits to the crystalline SrTiO₃. To separate the static, temperature independent, and the dynamic, thermally activated contributions to the mean squared disorder (σ^2) in the Ti-O bond lengths, the theoretical EXAFS spectrum was calculated assuming a regular, undistorted octahedral cage. The best fit value of the Ti-O bond length disorder σ^2 in amorphous SrTiO₃ ($0.015 \pm 0.003 \text{ \AA}^2$) was found to be much higher than in crystalline SrTiO₃ ($0.0027 \pm 0.0010 \text{ \AA}^2$), indicating strong static distortion within the TiO₆ cage in the amorphous sample. The second peak in the graph of the Fourier transform magnitudes of the EXAFS of the Ti edge of amorphous SrTiO₃ was found to be due to the contribution from the Ti-Ti bond with a length of $3.08 \pm 0.05 \text{ \AA}$. This Ti-Ti distance is typical for octahedra connected edge-to-edge (2.95–3.15 Å) and appears in a large variety of compounds [18–21]. In all these compounds, Ti ions must have strong off-center displacements, because were the edge-sharing octahedra undistorted (Ti in the center), the Ti-Ti distance would be only 2.76 Å. We modeled off-center displacements of Ti atoms in the [001], [011], and [111] directions of a cubic perovskite cell to match the experimentally observed Ti off-center displacement and σ^2 of the Ti-O bond. We excluded only those configurations that have an inversion symmetry (total dipole moment $\vec{p} = 0$). The results for the [100], [110], or [111] directions of the Ti atom displacements (Table I) were all consistent with the experiment. Therefore, a real displacement is, most probably, a combination of all three possible directions.

Evidence for the presence of an edge-to-edge connection between TiO₆ octahedra does not exclude the presence of the other types of contacts between TiO₆ octahedra, such as apex-to-apex and face-to-face. Since these types of connections are very common in various titanates [19,21,22], one should expect that they are present but that the Ti-Ti bond length disorder is too large to allow them to be reliably detected.

TABLE I. Experimental results and modeling of the bond lengths and disorder. The prefixes *c*, *a*, and *qa* denote crystalline, amorphous, and quasiamorphous phases. The symbol $\vec{d}||[hkl]$ denotes the direction of the Ti off-center displacement $[hkl]$.

Sample	Coordination Number	Ti-O Bond length, <i>R</i> (Å)	Bond disorder σ^2 (Å ²)	Coordination Number	Ti-Sr Bond length, <i>R</i> (Å)	Bond disorder σ^2 (Å ²)	Ti-Ti Bond length, <i>R</i> (Å)
Experiment							
<i>c</i> -SrTiO ₃	6	1.91(1)	0.0027(10)	8	3.37	0.012(4)	3.84(3)
<i>a</i> -SrTiO ₃	6	1.93(3)	0.015(3)	3.08(5)
<i>qa</i> -SrTiO ₃	6	1.91(6)	0.012(5)	3.1(1)
Modeling							
$\vec{d} [100]$	1, 4, 1	1.71, 1.97, 2.19, 1.96	0.0193	3.10
$\vec{d} [110]$	2, 2, 2	1.79, 1.97, 2.13, 1.96	0.0193	3.01
$\vec{d} [111]$	3, 3	1.82, 2.10, 1.96	0.0196	2.98

The XANES and EXAFS data presented above provide evidence that the structures of both the amorphous and quasiamorphous phases of SrTiO₃ comprise a random network of TiO₆ LBUs. In that respect, they are similar to the comparable phases of BaTiO₃ [3]. The transformation from the amorphous to the quasiamorphous phase involves major structural changes in the local environment of Sr but not of Ti. During this transformation, the octahedra are expected to be susceptible to alignment by the anisotropic strain induced by the temperature gradient, which is the major factor in the formation of the polar quasiamorphous phase [4]. Partial alignment of randomly connected, distorted TiO₆ octahedra was considered to be the origin of polarity in the quasiamorphous phase of BaTiO₃ [3]. This explanation is now suggested to suit SrTiO₃ as well. Therefore, one may conclude, based on this experimental evidence and theoretical predictions [2] that irrespective of whether a certain compound forms polar crystalline polymorphs, it can still form a polar noncrystalline phase. The macroscopic polarity of a quasiamorphous material is fundamentally different from that in crystalline inorganic pyroelectrics, where polarity is the direct result of a specific symmetry of the crystal lattice. In this view, our findings provide direct experimental verification of RN-LBU theory and prove that it can be used to search for other compounds that may form noncrystalline polar phases.

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